

# Polymer Solar Cells

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# Polymer Solar Cells

*Atef S. Iskander*

Polymer-based solar cells have emerged as one of the leading sources of clean and renewable energy, that have a wide variety of applications including the consumer electronics market and smart fabrics. Owing to their outstanding features as low-cost fabrication of large-area devices, low weight, flexibility, and tunability of chemical properties of the organic materials, intensive efforts have been made to develop the efficiencies of polymer solar cells (PSCs). Factors that influence the power conversion efficiencies as well as the stability of (PSCs), depend mainly on how to engineer both of the interface layer materials and the active layer materials. This article presents some of the recent advances in PSCs, including new interfacial layers, electron/hole transporting materials for single-junction and tandem PSCs, interconnecting layers, the technical challenges that need to overcome, and a hypothetical approach of lateral multijunction PSCs.

Keywords: Polymer solar cells, energy barriers, interfacial layers, oligothiophene molecules, packing mode.

## 1. Introduction

Solar cells play an important role in energy production, and constitute one of the most important renewable energy sources that convert solar energy in the form of sunlight to the more practical form of electricity. Organic photovoltaics (OPVs) or organic solar cells (OSCs), a subset of these energy sources, are made of thin film of organic semiconductor materials, and have received exceptional attention as a promising alternative to their inorganic counterparts for the generation of affordable, clean, renewable energy. This technology paves the way to employ them, in particular organic polymeric-based solar cells (PSCs), in a wide range of applications, owing to their outstanding properties, including economic viability of large-scale power generation; low weight; mechanical flexibility; and great functional-tunabilities. They can be bend or curve around structures or even be incorporated into clothing.

In the recent scenario, power conversion efficiencies have been achieved up to 17% for both single- and tandem-junction OSCs.<sup>1</sup> Researchers are interesting to push the efficiency to reach a new record by elaborating and optimizing both active layer material properties and device architectures.<sup>2</sup> This article

presents the basic concepts of PSCs; some of the recent advances in their constituent components; and discuss some major challenges in achieving higher efficiency as well as a proposed approach of lateral multijunction PSCs.

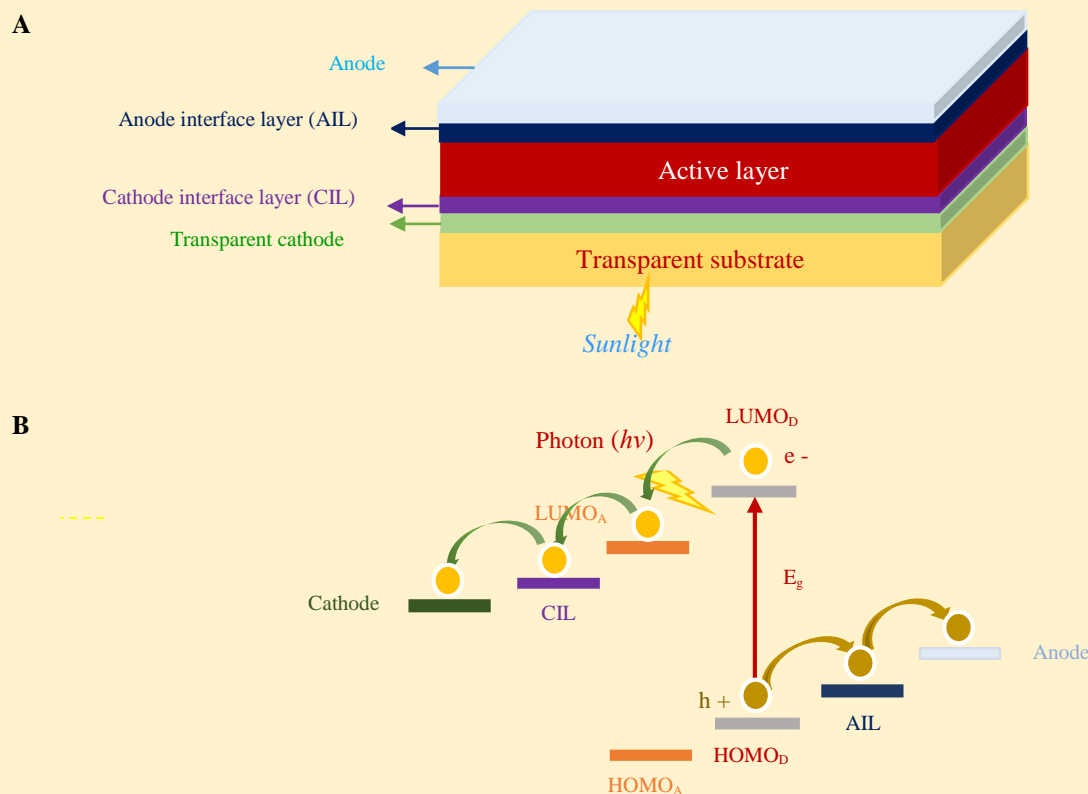
## 2. Basic concepts of polymer solar cells

One of the most attractive features of PSCs is how easily they can be fabricated. A typical bulk-heterojunction polymer solar cell consists of a photoactive layer of bulk-heterojunction (BHJ) of donor and acceptor materials that is sandwiched between two electrodes. This blend active layer of the donor and acceptor materials form an interpenetrating three-dimensional (3D) bicontinuous network. The bottom electrode is a modified transparent metal oxide with a low work-function, such as indium tin oxide (ITO), which allows the light to pass through and acts as the cathode. The top contact is a less air-sensitive metal with a high work-function, such as gold or silver, which acts as the anode. In order to enhance the collection efficiencies of holes and electrons on the anode and cathode, respectively, interfacial materials with suitable work-function are inserted between the active layer and electrodes (Figure 1 A). This architecture is in the case of the inverted devices, which differs from the conventional devices in the configuration. The conventional devices suffer from many drawbacks including rapid degradation, poor lifetime as a result of the acidic and hydrophilic nature of the active layer materials as well as the sensitivity of low work-function metal anodes in these devices to oxygen and moisture.<sup>3,4</sup>

Concerning of the mechanism of the PSCs, the donor polymer is the active component in the cell, that absorbs light, generates excitons, and separates into holes and electrons in the highest occupied molecular orbital (HOMO) of the donor, and the lowest unoccupied molecular orbital (LUMO) of the acceptor respectively. The acceptor material assists in exciton dissociation where the hole remains on the donor molecule and the electron is transferred to the acceptor. After dissociation, the separated charges are transported within the respective phases of the active layer, until they are collected at the opposite electrodes (Figure 1 B).

In the case of tandem PSCs, an interconnecting layer is used between the active layers to connect the subcells and to extract holes and electrons from them, and then to complete the charge recombination within them. Thus, the performance of tandem devices depends to a great extent on the optimal choices and properties of the interconnecting layer materials.

Generally, the photovoltaic power-conversion efficiency ( $\eta$ ) is determined by a set of parameters which includes the short-circuit current density ( $J_{sc}$ ), the open-circuit voltage ( $V_{oc}$ ), the maximum operating power ( $P_{max}$ ), and the fill factor ( $FF$ ) (see Table 1 for definitions). These parameters play a pivotal role in affecting device performance.



**Figure 1.** A) Schematic inverted single junction polymer bulk-heterojunction architecture. B) Schematic illustration of energy level diagrams and charge transfer process in an inverted single junction BHJ cell.

One of the major challenges in achieving higher efficiency in PSCs is how to realize efficient extraction of holes and electrons to their respective electrodes. In fact, the driving force behinds the execution of such a goal relying on the mature choice of suitable interfacial layers as charge-extracting constituents in single-junction and as charge recombination layers in tandem PSCs.<sup>5</sup> A suitable interfacial layer can be used (i) to adjust the energy level alignment at the electric contact/active-layer interfaces;<sup>6</sup> (ii) to modify light absorption in the active layer through introducing optical spacer and plasmonic effects;<sup>7</sup> (iii) to define the polarity of electrodes and to improve charge selectivity;<sup>8</sup> (iv) to tune the morphology of the active layer through regulating surface energy;<sup>9</sup> (v) to architect the built-in electric field;<sup>10</sup> and (vi) to improve interfacial stability between the active layer and electrodes.<sup>11</sup> Indeed, the interfacial materials have a direct and important impact on device efficiency and stability. In the next section, a brief overview on these interfacial materials is presented.

**Table 1.** Glossary of terms used

The diode equation	<p>An expression for the current through diode as function of voltage.</p> $I = I_o (e^{qV/kT} - 1)$ <p>where:  <math>I</math> = the net current flowing through the diode;  <math>I_o</math> = dark saturation current, the diode leakage current density in the absence of light;  <math>V</math> = applied voltage across the terminals of the diode;  <math>q</math> = absolute value of electron charge;  <math>k</math> = Boltzmann's constant; and  <math>T</math> = absolute temperature (K).</p>
The I-V curve of a solar cell	<p>The superposition of the I-V curve in the dark with the light generated-current. Illumination shifts the I-V curve down into the fourth quadrant where power can be extracted from the diode. Illuminating a cell adds to the normal dark current in the diode so that the diode equation becomes:</p> $I = I_o [ \exp (qV / nkT) - 1 ] - I_L \quad \text{where } I_L = \text{light generated current.}$
The short-circuit current ( $I_{sc}$ )	The current through the solar cell when the voltage across the solar cell is zero. $I_{sc} \approx I_L$
The short-circuit current density ( $J_{sc}$ )	The maximum current density that is obtained when there is no voltage across the solar cell. ( $J_{sc}$ in mA/cm <sup>2</sup> )
The open circuit voltage ( $V_{oc}$ )	<p>The maximum voltage that is obtained when no current is generated by the solar cell.</p> $V_{oc} = nkT/q \ln [ (I_L / I_o) + 1 ]$
The fill factor (FF)	<p>The ratio of the maximum operating power (<math>P_m</math>) to the maximum extractable power from an ideal solar cell, which would be the product of the device area <math>A</math>, <math>V_{oc}</math>, and <math>J_{sc}</math>.</p> $FF = P_m / A V_{oc} J_{sc}$
The power conversion efficiency ( $\eta$ )	<p>The ratio of the maximum operating power <math>P_m</math> to the input power of the incident light on the solar cell.</p> $\eta = V_{oc} J_{sc} FF / I_{in} \quad \text{where } I_{in} = \text{incident light intensity}$

### 3. Cathode interfacial layer

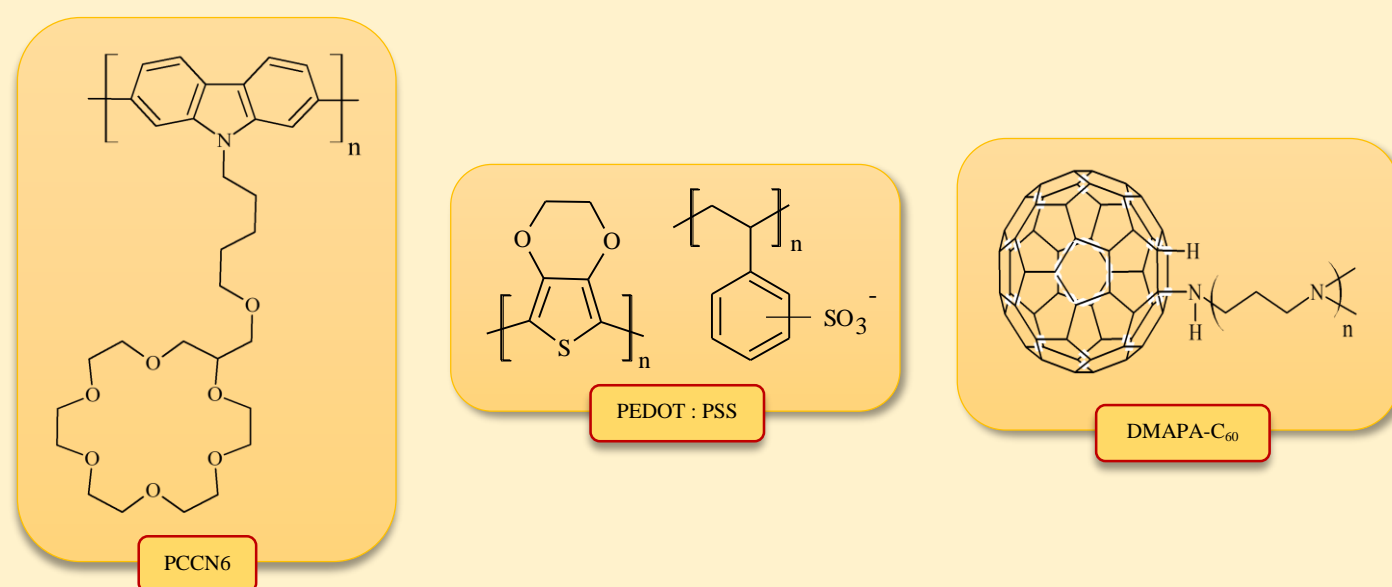
Cathode interfacial layer is made from n-type electron-transporting molecules with low work-function to match with LUMO levels of acceptor molecules in the active layer for charge extraction, good electron-transporting/hole-blocking properties for charge transportation, and better compatibility between cathode and active layers for reducing interface defects and energy losses. This layer should be transparent for light

transmittance. In order to understand the control property of these electron-transporting molecules which affects the device performance, this section aims to shed light on some of these molecules.

### 3.1. Polymers and small molecules

A huge number of electron-transporting molecules have been developed, including polymers and small molecules. The feature of the incorporation of polymers and organic molecules in PSCs is that their structures can be easily tuned towards both suitable energy levels and optical/electronic properties. In fact, organic cathode interfacial layers can induce an interface dipole pointing from cathode to the active layer in the device geometry as a result of intermolecular dipole moment and the ability to form self-assembled monolayers, which, in turn, reduces effectively the work-function of cathodes and enhancing the built-in potential of PSCs.<sup>12</sup>

Water/alcohol soluble conjugated polymers are effective cathode interfacial layers for PSCs applications. These materials can efficiently adjust the work-function of cathodes by forming an interfacial dipole between cathode and the active layer, enhancing charge transport. For example, the polymer (PCCn6) with electron rich bridge nitrogen atom in the main chain exhibited good performance in power conversion efficiency promotion, which can induce higher interfacial dipole for improved  $V_{oc}$  and promote absorption of the active layer through its optical interference effect for redistribution of the optical electric field. (Figure 2).<sup>13</sup>



**Figure 2.** The structure of some polymers and a carbon-based molecule.

### 3.2. Carbon-based molecules

Another class of cathode interfacial layer components is carbon-based molecules, such as fullerene, carbon nanotube, and graphene including their derivatives. They have many benefits for PSCs with their higher conductivity, good structural stability, and tunable functionality. For instance, fullerene derived molecules have unique virtues of being structurally similar to the fullerene acceptors, which can smoothly bridge electrons extracting/transporting from the fullerene acceptor to the cathode. The solution-processable amine group functionalized fullerene derivative, DMAPA-C<sub>60</sub>, is a versatile cathode interfacial layer for increasing the performance of different polymer/fullerene devices (Figure 2).<sup>14</sup>

## 4. Anode interfacial layers

In order to match the HOMO levels of the donor materials in the active layer, the hole-transporting molecules of anode interfacial layer should have high work-function to facilitate hole-extraction in contrast to the electron-transporting materials of cathode interfacial layer, which have low work-function for electron collection. The performance of PSCs is influenced by how efficient is the transport of holes that minimizes series of resistances. Among the hole-transporting molecules of anode interfacial layer, organic conductive polymers, such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) – a polymer mixture of two ionomers - (PEDOT:PSS) (Figure 2), which is widely used in PSCs owing to its high conductivity and easy solution-processing. In addition, the convenient work-function of PEDOT:PSS (~ 5.1 eV) matches with a wide range of polymer donors to form ohmic contact at the anode/active layer interface.<sup>15</sup> On the other hand, PEDOT:PSS suffers from the acidic and moisture sensitive nature that significantly affects the stability of devices. Therefore, incorporation of metal nanoparticles such as gold (Au), silver (Ag) NPs or Au@Ag nanocomposites into PEDOT:PSS film improves its performance in PSCs. Such improvement is attributed to the localized surface plasmon resonance effect.

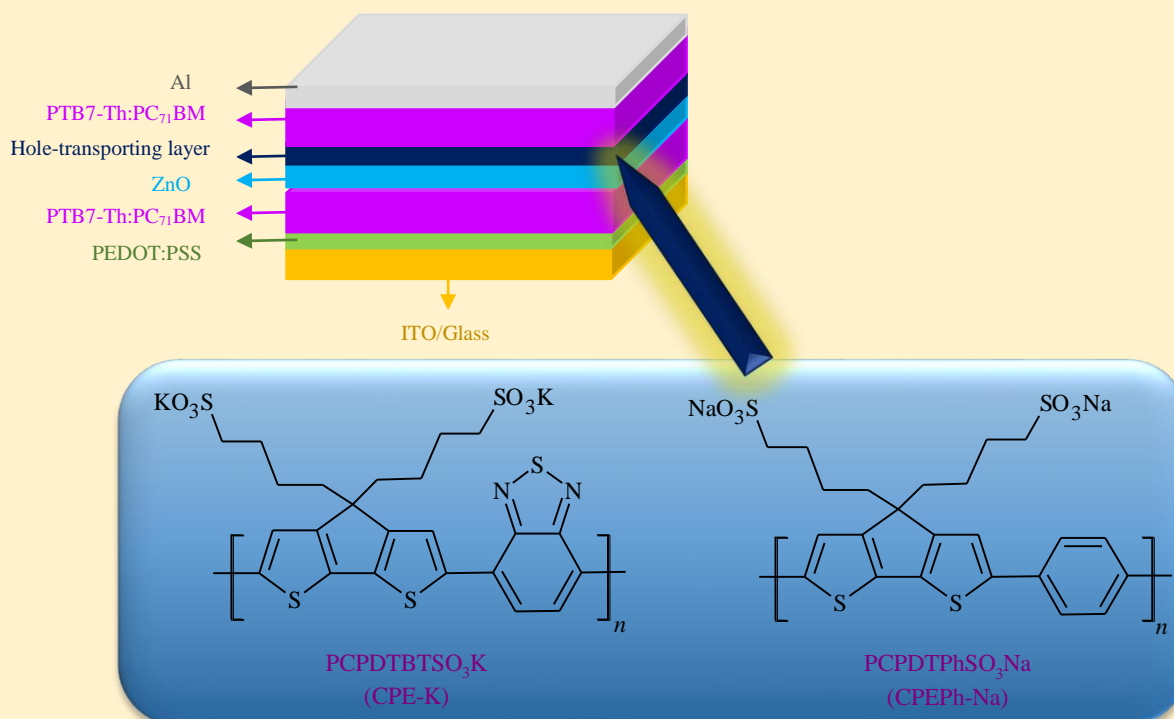
## 5. Interconnecting layer materials for tandem PSCs

The interconnecting layer materials play an important role in tandem PSCs, as they connect the neighboring subcells. Thus, they function as a charge recombination zone to complete the circuit. In fact, the open circuit voltage is determined by summing  $V_{oc}$  of the individual subcells, while the overall  $J_{sc}$  is determined by the subcell with the smaller current.

Good interconnecting layers should have: (i) perfect vertical conductivity to reduce electrical losses; (ii) high transmittance to minimize light absorption; (iii) energetic to facilitate charge recombination; and (iv) low surface roughness to avoid interrupting the deposition of adjacent subcells.<sup>16</sup> In order to fulfill these



requirements, many interconnecting layers for both conventional and inverted tandem PSCs were developed based on the insertion of a conductive layer between electron- and hole-transporting layers. The electron-transporting layer and hole-transporting layer are employed for electron and hole collection, respectively, where the single intermediate conductive layer is served as charge recombination center. Indeed, thin film metals, such as Au, Ag, or Al, are used as highly conductive layer for conventional tandem PSCs, which can realize the desired functions of high transparency, minimized voltage losses, and serving as an optical spacer to match the current between the subcells. Furthermore, the interconnecting layer based on a metal oxide and highly self-doped conjugated polyelectrolytes (CPEs) have been demonstrated to have good electric conductivity, making them potentially strong candidates for solution-processed PSCs applications. CPEs contain a  $\pi$ -conjugated electronic structure with pendant ionic functionalities, in which the pendant cationic functionalities lower both the energies of HOMO and LUMO levels, thus stabilizing the radical anions in the conjugated backbones. For instance, highly self-doped CPEs such as 4,4-bis-alkyl-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene and 2,1,3-benzo-thiadiazole structural units (CPEPh-Na) and (CPE-K) were demonstrated as effective *p*-type hole-transporting layers to combine with ZnO electron-transporting layer for solution-processed tandem PSCs (Figure 3). The work-function of hole-transporting layers plays a crucial role in the hole extraction and affect the charge recombination within the interconnecting layer. Thus, the ZnO/CPEs have been proved to be efficient interconnecting layers, where showed better performance with enhanced  $V_{oc}$  and  $FF$ .<sup>17</sup>



**Figure 3.** A schematic tandem device with an interconnecting layer of ZnO/CPE, and the structures of CPE-K and CPEPh-Na polymers as hole-transporting layers.

In inverted OSCs based on PTB7 as a donor and PC<sub>71</sub>BM as an acceptor, DMAPA-C<sub>60</sub> showed much better device performance compared with their ZnO counterparts.<sup>18</sup> In this inverted organic solar cells, DMAPA-C<sub>60</sub> serve as cathode buffer layers to modify the transparent cathode ITO.

## Technical challenges

Another significant advantage of PSCs is that they do not require directly incident sunlight to generate power; they respond well to indirect and low-light conditions, such as on a cloudy day. So, PSCs can be used in a variety of applications ranging from consumer electronics market and smart fabrics to building integrated photovoltaics market, or other grid applications.

Such huge applications require a significant improvement in PSCs efficiency to reach a new record, beyond 25% with product lifetimes of at least 18-20 years. In order to realize such a goal, one of the major challenge is the lack of optimal absorber polymers with the desired properties. Therefore, new polymer development efforts must be focus on: (i) improving the absorption edge to be enable in the infrared and near infrared regions of the solar spectrum to utilize sunlight more efficiently and effectively; (ii) optimizing band offset between donor and acceptor molecules to reduce energy loss during the exciton separation; (iii) tuning the energy level in donor/acceptor polymers to achieve a higher  $V_{oc}$ ; (iv) enhancing  $\pi$ - $\pi^*$  stacking or the regularity of molecular structure within polymers to achieve higher charge carrier mobility; and (v) modifying the morphology to obtain higher molecular crystallinity. Another challenge, that needs to be overcome, is the development of manufacturing processes, which would enable production of PSCs at high throughput, high yield, and low cost.

Remarkably, no type of lateral polymer multijunction solar cell has been reported. In fact, the reported PSCs are stacking multijunction cells, that are connected in series. As a hypothetical approach to improve efficiency values, the utilization of different arrays of optimized polymers of varying bandgap may allow to split the incident light in different lateral spatial locations matching with the location of each array of the optimized bandgap. Consequently, this may allow to reduce energy loss and to extract the current from each array separately.

Would this approach allow to integrate polymers implanted with metal nanoparticles, such as gold, silver, or phosphorus NPs, in their construction?

## 6. Conclusion

Large progress has been made in improving the power conversion efficiency of polymer solar cells. Although this progress is impressive, such performance has to be further improved for larger scale applications. PSCs has the potential to realize higher efficiencies through optimizing energetic levels,

optical and electrical properties of both the absorber layers and interfacial layers, and long-term stable devices. Among the challenges is the non-radiative recombination of photoinduced charge carriers, that will need to overcome. Besides, materials with a high ordered morphology, better charge transport properties and less electronic traps will be needed for such improving.

## References

- 1) L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, *Science*, **2018**, 361 (6407), 1094-1098.
- 2) N. Li, D. Baran, G. D. Spyropoulos, H. Zhang, S. Berny, M. Turbiez, T. Ameri, F. C. Krebs, C. J. Brabec, *Adv. Energy Mater.*, **2014**, 4, 1400084.
- 3) M. Jørgensen, K. Norrman, F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, **2008**, 92, 686.
- 4) Z. G. Yin, Q. D. Zheng, *Adv. Energy Mater.*, **2012**, 2, 179.
- 5) M. Vasilopoulou, E. Polydorou, A. M. Douvas, L. C. Palilis, S. Kennou, P. Argitis, *Energy Environ. Sci.*, **2015**, 8, 2448.
- 6) J. Subbiah, G. Sarasqueta, F. So, H. Ding, Y. Gao, *Appl. Phys. Lett.*, **2009**, 95, 093304.
- 7) S. W. Baek, G. Park, J. Noh, C. Cho, C. H. Lee, M. K. Seo, H. Song, J. Y. Lee, *ACS Nano*, **2014**, 8, 3302.
- 8) D. Bilby, B. Frieberg, S. Kramadhati, P. Green, J. Kim, *ACS Appl. Mater. Interfaces*, **2014**, 6, 14964.
- 9) J. R. Manders, S. W. Tsang, M. J. Hartel, T. H. Lai, S. Chen, C. M. Amb, J. R. Reynolds, F. So, *Adv. Funct. Mater.*, **2013**, 23, 2993.
- 10) Y. B. Yuan, T. J. Reece, P. Sharma, S. Poddar, S. Ducharme, A. Gruverman, Y. Yang, J. S. Huang, *Nat. Mater.*, **2011**, 10, 296.
- 11) M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.*, **2012**, 24, 580.
- 12) S. Chem, C. Carbonera, A. Bernardi, N. Camaioni, *Energy Environ. Sci.*, **2011**, 4, 285.
- 13) Y. -L. Li, Y. -S. Cheng, P. -N. Yeh, S. -H. Liao, S. -A. Chen, *Adv. Funct. Mater.*, **2014**, 24, 6811.
- 14) Z. Zhang, H. Li, B. Qi, D. Chi, Z. Jin, Z. Qi, J. Hou, Y. Li, J. Wang, *J. Mater. Chem. A*, **2013**, 1, 9624.
- 15) H. L. Yip, A. K. Y. Jen, *Energy Environ. Sci.*, **2012**, 5, 5994.
- 16) Z. Yin, J. Wei, Q. Zheng, *Adv. Sci.*, **2016**, 3, 1500362.
- 17) H. Q. Zhou, Y. Zhang, C. K. Mai, S. D. Collins, G. C. Bazan, T. Q. Nguyen, A. J. Heeger, *Adv. Mater.*, **2015**, 27, 1767.
- 18) Y. Wang, H. Cong, B. Yu, Z. Zhang, X. Zhang, *Materials*, **2017**, 10, 1064.

# Snapshots of some topics of interest of recent notable advances in chemistry

*Atef S. Iskander*

*Managing Director / Founder*

# Novel Functionalized Ligands for Multicomponent Metal-Organic Frameworks

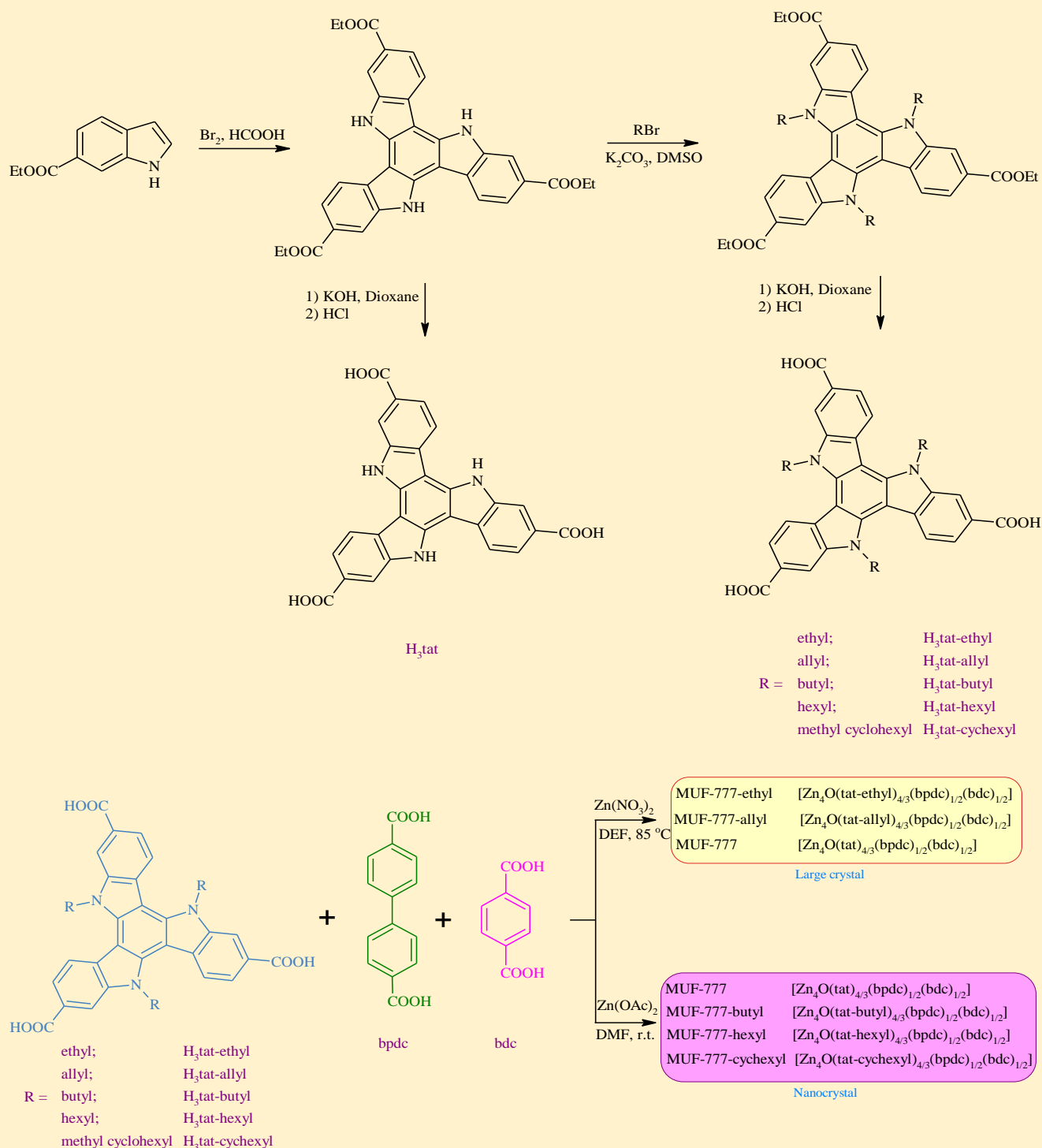
A new isorecticular series of multicomponent metal-organic frameworks is highlighted, which based on new tritopic triazatruxene ligands along with biphenyl-4,4'-dicarboxylic acid; terephthalic acid; and  $Zn_4O$  clusters.

The architecture of metal-organic frameworks (MOFs) depends to a large extent on how precise to control the coordination of the organic components within extended crystalline structure. This can be achieved by the successful application of the isorecticular principle, where the functionality and metrics of an extended porous structure can be altered without changing its underlying topology.

Telfer and co-workers reported the preparation of a series of multicomponent MOFs, which incorporated tritopic ligands based on a rigid, electron-rich  $C_3$ -symmetric triazatruxene core functionalized with tricarboxylic acid,  $H_3tat$ , along with biphenyl-4,4'-dicarboxylic acid (bpdc); terephthalic acid (bdc); and  $Zn_4O$  clusters (Scheme).

Under solvothermal conditions, the quaternary MOFs, MUF-777; MUF-777-ethyl; and MUF-777-allyl, were obtained as large crystals, where the other isorecticular, MUF-777-butyl; MUF-777-hexyl; and MUF-777-cyhexyl were obtained at room temperature as nanocrystals. (MUF = Massey University Framework)

Derivatization of  $H_3tat$  with various substituents on its nitrogen centers can lead to new ligands with different electronic and steric properties, which can be employed to tune MOF features.



**Scheme.** The preparation of tat-based ligands, and the employed synthesis conditions for MOFs.

## Review

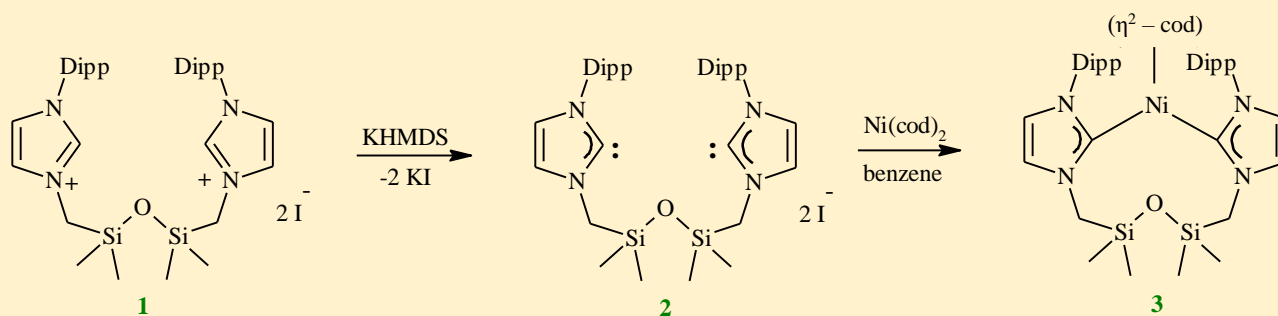
A. Alkas, J. Cornelio, S. G. Telfer, *Chem. Asian. J.*, **2019**, *14*, 1167-1174.

## Enhancing the Lewis Basicity of a Transition Metal by Chelating with Smart Ligands

The preparation of T-shaped nickel(0) germylene complex chelating with bis(NHC) ligand is described. The complex has a significant multiconfigurational character, while the unusual Ni-Ge bonding is formed through  $\sigma$ -donation from Ni orbitals to Ge.

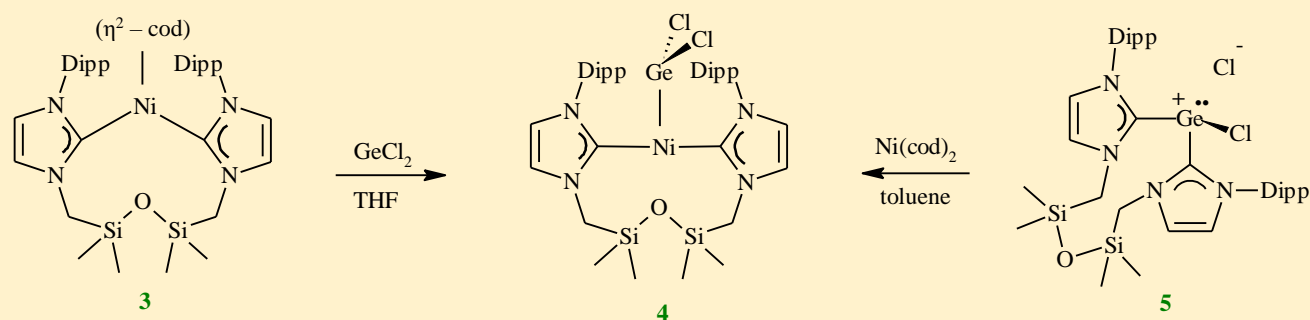
The Lewis basicity of transition metals constitutes a crucial factor in the construction of their complexes. Among these complexes are the dicoordinate complexes of nickel(0) ( $\text{Ni}^0$ ) with N-heterocyclic carbene (NHC) ligands,  $(\text{NHC})_2\text{Ni}(0)$ , which are considered as powerful precatalysts in bond-forming transformations, as well as oxidative addition reactions. Thus, the design of such complexes is an attractive goal owing to their linearity and high reactivity. In this context, Roesler and co-workers reported a synthetic procedure for a T-shaped nickel ( $\text{Ni}^0$ )-germylene (Ge) complex incorporating bis(NHC) ligand, which has the ability to accommodate a wide range of bite angles.

The chelating bis(NHC) ligand **2** was reacted with bis(1,5-cyclooctadiene)nickel(0),  $\text{Ni}(\text{cod})_2$ , to give  $\eta^2$ -cyclooctadiene complex **3** (Scheme 1).



**Scheme 1.** Preparation of ligand **2** and its complex **3**; KHMSD = potassium bis(trimethylsilyl)amide; Dipp = 2,6-di-isopropyl-phenyl;  $\text{Ni}(\text{cod})_2$  = bis(1,5-cyclooctadiene)nickel(0).

The nickel-germanium complex **4** was prepared either by the substitution reaction of **3** with  $\text{GeCl}_2$ , or by transmetalation of **5** with  $\text{Ni}(\text{cod})_2$ , followed by coordination of the extruded metalloid fragment to Ni in a casting-like reaction (Scheme 2).



**Scheme 2.** Preparation of T-shaped  $\text{Ni}^0$  complex **4**;  $\text{GeCl}_2$  = germanium dichloride.

Complex **4** exhibits a T-geometry, which is unprecedented for  $\text{Ni}^0$ . Its unusual Ni-Ge bonding is envisaged as a dative  $\text{Ni}^0 \rightarrow \text{Ge}^{\text{II}}$  interaction with two components: i) a weak  $\sigma$ -donation from  $\text{Ni}_{3d}$  to  $\text{Ge}_{4p}$ , representing a minor contribution, and ii) a one-electron  $\sigma$ -donation from  $\text{Ni}_{4s-4p}$  to  $\text{GeCl}_2$ .

This work demonstrated the influence of ligands on the nickel(0) Lewis bases, which can promote its reactivity to align the more basic platinum analogues. In addition, it highlights the important role of the  $d^9s^1$  electronic structure in the chemistry of metal complexes that typecast as  $3d^{10}$ .

## Review

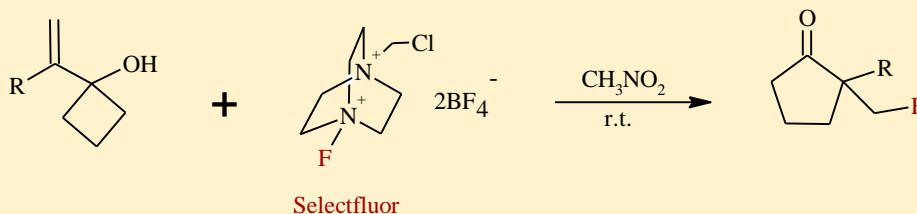
C. Gendy, A. Mansikkamäki, J. Valjus, J. Heidebrecht, P. Ch-Y. Hui, G. M. Bernard, H. M. Tuononen, R. E. Wasylshen, V. K. Michaelis, R. Roesler, *Angew. Chem. Int. Ed.*, **2019**, 58, 154-158.



# Ring Expansion via Radical Fluorination/1,2-Alkyl Migration Cascade Process

A practical synthetic procedure for fluoromethyl-substituted cyclopentanone derivatives from alkenyl cyclobutanols is described.

The synthesis of  $\beta$ -fluoromethyl cyclopentanones was accomplished via the coupling reaction of alkenyl cyclobutanols with Selectfluor, as fluorine radical source, under mild condition (Scheme).



**Scheme .** Synthesis of fluoromethyl-substituted cyclic ketone derivatives.

The strategy of this reaction is based on radical-mediated difunctionalization of alkenes. As a radical source, Selectfluor reacted with allylic alcohol derivatives to undergo radical fluorination/1,2 alkyl migration cascade in nitromethane at room temperature. Various alkenyl cyclobutanols with electron-donating or electron-withdrawing substituted-aryl and naphthyl groups afforded the corresponding migration products with moderate to high yields (67-98%). This reaction features a broad substrate scope

## Review

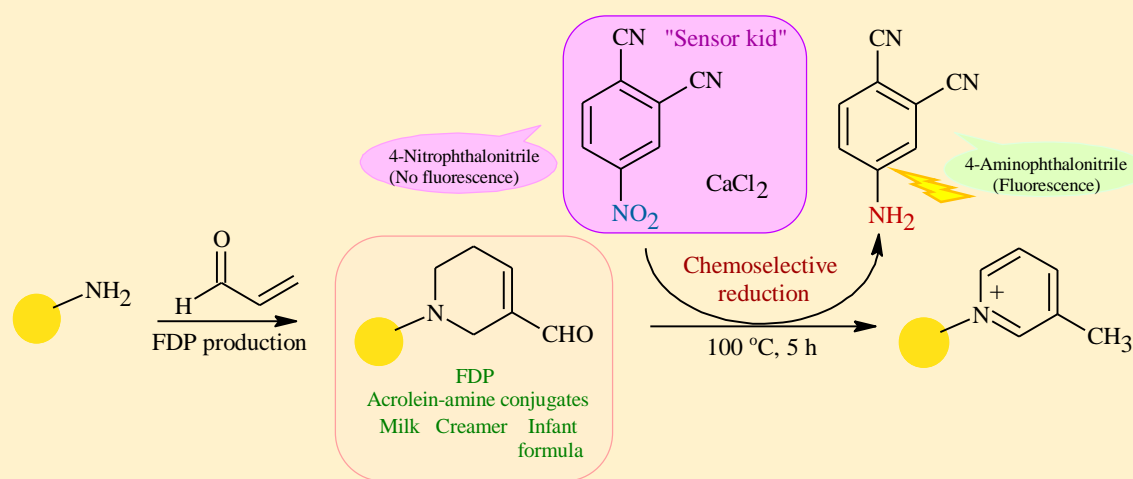
Y. Kim, D. Y. Kim, *Asian. J. Org. Chem.*, **2019**, *8*, 679-682.

## Chemistry-Based Method for Detection of Acrolein-Amine Conjugates

The highly reactive and toxic acrolein reacts readily with various functional groups of proteins or nucleobases, e.g. amino, thiol, and hydroxyl groups, forming acrolein adducts, e.g., 3-formyl-3,4-dehydropiperidine (FDP) adduct. A reduction-based sensor kit was employed to detect the amount of FDP as the preferential acrolein-amine conjugates in milk products.

Acrolein is a highly toxic unsaturated aldehyde, that is well recognized as a hazard to human health. It is highly reactive compound to various functional groups, and can readily conjugate with food materials, e.g. forming 3-formyl-3,4-dehydropiperidine (FDP) adduct with lysines of proteins, a similar modification to advanced glycation end-products.

FDP is considered as a biomarker to diagnose acrolein-related diseases. It was found that FDP can reduce electron deficient nitroarenes in high yields at 100 °C in the presence of excess CaCl<sub>2</sub> as a Lewis acid promoter. Based on this, the non-fluorescent and inexpensive 4-nitrophthalonitrile probe was converted to the corresponding fluorescent aniline (Figure).



**Figure.** Sensor kit for detecting FDP from milk products.

The results pointed out to: i) the produced acrolein-amine conjugates in milk products depended on pasteurization, high temperature treatment, and contents of animal fats; and ii) the concentration of FDP

significantly increased when heated to 80-100 °C under the conditions of hot milk, coffee, and cooking food.

#### Review

A. Kishimoto, S. Nomura, K. Tanaka, *Bull. Chem. Soc. Jpn.*, **2019**, 92, 1018-1023.